



# Oxygen-vacancy induced structural changes of Co species in $\text{CoAl}_2\text{O}_4$ spinels for $\text{CO}_2$ hydrogenation

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## ARTICLE INFO

### Keywords:

$\text{CO}_2$  hydrogenation

Selectivity

$\text{CoAl}_2\text{O}_4$

Oxygen vacancies

Mechanism

## ABSTRACT

Promotional effects of oxygen vacancies of spinel catalysts in  $\text{CO}_2$  hydrogenation are reported in early works, but the mechanistic origins remain elusive. Here,  $\text{CoAl}_2\text{O}_4$  spinels with varying numbers of oxygen vacancies are deliberately designed by a sol-gel method and different post-treatments. By combining catalytic testing, advanced electron microscopic and spectroscopic characterizations, and computational studies, the unusual oxygen vacancy-dependent catalytic behaviors are rationalized. Our work reveals that i) perfect spinel crystals possessing least oxygen vacancies can effectively constrain the  $\text{Co}^{2+}$  species at working conditions that are less active but selective to CO; and ii) vacancy-rich spinels promote both  $\text{H}_2$  and  $\text{CO}_2$  activations and  $\text{COOH}^*$  formation, explaining the higher hydrogenation activity, but overwhelming vacancies cause  $\text{Co}^{2+}$  reduction and promote direct  $\text{CO}_2$  dissociation to  $\text{CO}^*$  and deep hydrogenation to  $\text{CH}_4$ . These molecular-level understandings reinforce the idea of proper design of oxygen vacancies to achieve activity-selectivity balance.

## 1. Introduction

Spinel catalysts of diverse compositions have revealed fascinating prospects among various catalytic reactions [1]. In heterogeneous catalysis, oxygen vacancies play an essential role in determining the catalytic performance. For instance, numerous literatures demonstrate that oxygen vacancies on the surface of spinels are one of the most key defects which can act as the active sites in a range of catalytic reactions, such as CO and  $\text{CO}_2$  hydrogenation [2,3], toluene and methane oxidation [4,5], biomass conversion and  $\text{N}_2\text{O}$  decomposition [6,7], etc. Furthermore, the presence of oxygen vacancies on the surface often dramatically changes the adsorption and subsequent reactions of diverse adsorbates considerably, and then affect product selectivity [8–10]. However, full understanding of the crucial functions of oxygen vacancies in the reaction mechanism (e.g., reaction route and

rate-determining step) is severely lacking [11,12]. Deep explorations in this field will shed light on catalytic reaction-promoting effect of oxygen vacancies, which is beneficial to rational catalyst design and implementation for novel catalytic technologies [13,14].

Using  $\text{CO}_2$  as a cheap and abundant  $\text{C}_1$  raw material to synthesize high-value chemicals could not only alleviate the adverse environmental impacts, but also assist in resolving the energy crisis [15–18]. The syngas ( $\text{CO} + \text{H}_2$ ) obtained by reverse water gas shift (RWGS) reaction is a crucial raw ingredient for chemicals, which could be used to produce an array of liquid fuels and platform chemicals through existing mature processes such as Fischer-Tropsch synthesis and methanol synthesis [19–21]. Usually, the RWGS reaction is accompanied with the formation of  $\text{C}_1$  products such as  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  [22,23]. Methanation of  $\text{CO}_2$  is a significant catalytic approach to recycling  $\text{CO}_2$  emissions into usable fuels with promising commercial applications and environmental

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benefits [24–26]. Spinel s were widely used as catalyst and support in CO<sub>2</sub> hydrogenation reactions due to the unique properties. For instance, MgAl<sub>2</sub>O<sub>4</sub> could serve as a dopant matrix to stabilize small Ni particles, allowing it to exhibit good selectivity in CO<sub>2</sub> methanation reactions [27]. CuAl<sub>2</sub>O<sub>4</sub> also exhibits excellent stability in RWGS reaction [28]. ZnAl<sub>2</sub>O<sub>4</sub> could be used as a carrier to inhibit sintering of dual-site Cu/ZnAl<sub>2</sub>O<sub>4</sub> in CO<sub>2</sub> hydrogenation to methanol [29]. Due to the intricate nature of the CO<sub>2</sub> hydrogenation reaction network, it is critical to understand the mechanistic origins of CO<sub>2</sub> hydrogenation and rationally regulate the catalyst structure in order to generate a single product with high selectivity [30,31].

Oxygen vacancy design of metal oxide catalysts has been emerging as a promising strategy to regulate their catalytic performance in CO<sub>2</sub> hydrogenation. In this aspect, valuable insights have been gathered from the previous studies. The oxygen affinity of oxygen vacancies provides additional adsorption and activation sites for CO<sub>2</sub>, which could improve the catalytic activity of CO<sub>2</sub> hydrogenation [13]. The highly inverted spinel catalysts with rich oxygen vacancies were reported to greatly increase the catalytic activity [32]. In addition, oxygen vacancies could also stabilize other active sites for coordinated directional catalysis [33], or promote the generation of stable reaction intermediates such as formates and methoxy species, which were then further hydrogenated to methanol [34] and methane [35], or dissociated to CO [10]. These earlier works mainly focused on improving CO<sub>2</sub> adsorption and activation. Since catalytic reactions often occur around oxygen vacancies with higher CO<sub>2</sub> adsorption capacity, the increased oxygen vacancies may also alter the activation of H<sub>2</sub>. A recent study by Fu et al. [36] showed that excessive H<sub>2</sub> activation causes H<sub>2</sub> spillover to non-vacancies and thus affects the catalytic route. Therefore, it is particularly critical to assess the impact of oxygen vacancies on the catalyst structures and the underlying reaction mechanisms.

To tackle the above-mentioned challenge, three representative CoAl<sub>2</sub>O<sub>4</sub> spinel catalysts with different numbers of oxygen vacancy structures were prepared through combining a sol-gel method with different post-treatments. The microstructures and in particular the oxygen vacancies of the developed catalysts were deeply analyzed by a spectrum of advanced characterization techniques. The steady-state catalytic CO<sub>2</sub> hydrogenation performances were also fully evaluated and substantiated by in situ spectroscopic and computational studies. Our results showed that the CoAl<sub>2</sub>O<sub>4</sub> spinels with perfect crystal facets and least oxygen vacancies could effectively constrain and stabilize the Co<sup>2+</sup> species in the RWGS reaction, consequently delivering nearly 100% CO selectivity for 100 h even at 500 °C. On the contrary, the analogues with increasing oxygen vacancies facilitated H<sub>2</sub> chemisorption and Co<sup>2+</sup> reduction, which shifts the hydrogenated product to CH<sub>4</sub>. These divergent catalytic behaviors of the spinel catalysts and the underlying hydrogenation mechanisms were discussed and rationalized by joint in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFT) and density functional theory (DFT) studies.

## 2. Experimental

### 2.1. Catalyst preparation

The Co-Al spinels were prepared by a low-temperature sol-gel method (Fig. S1). First, 0.04 mol Al(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O (Aladdin, 99.9%) and 0.02 mol Co(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (Aladdin, 99.9%) were fully dissolved into 20 mol ethanol (Tianjin Damao Chemical Reagent, 99.7%). The solution was added into 8 mol propylene oxide (Sinopharm Chemical Reagent, 99.0%) at 50 °C with continuous stirring until a Co-Al gel was formed. The gel was then aged for 8 h and dried at 80 °C for 12 h. The dried material was heated at a tube furnace (800 °C, 5 °C/min, 5 h) under either N<sub>2</sub> or air atmospheres, and the derived solids were designated as SPN and SPA, respectively. Additionally, the SPA catalyst was treated by alkali washing to create further oxygen vacancies [32]. The alkaline-treated catalyst was prepared by treating 1.0 g of SPA with 50

mL of a 0.5 M aqueous NaOH solution at 50 °C for 1 h. The resulting suspension was centrifuged, washed thoroughly and then dried at 80 °C for 12 h. The obtained sample was recorded as SPA-NaOH. Lastly, SPN was heated at 600 °C in air (5 °C/min, 5 h) to generated another sample denoted as SPN-A.

### 2.2. Catalyst characterization

#### 2.2.1. Structural characterization

Thermogravimetric measurements were performed on a STA449F5-Thermostat thermal analyzer in air or N<sub>2</sub> atmospheres with a heating rate of 10 °C/min. Scanning electron microscopic (SEM) images and energy dispersive spectroscopy (EDS) mappings were taken on a JSM-7800 F microscope. High-resolution transmission electron microscopic (HRTEM) images were obtained using a JEOL JEM-2100 electron microscope with 200 kV accelerating voltage. Scanning-transmission electron microscopy (STEM) and the corresponding high-resolution elemental mapping of energy dispersive X-ray (EDX-mapping) images were acquired on a JEM-ARM200F STEM/TEM instrument equipped with Super X EDS, with an instrument resolution of 0.08 nm and an accelerating voltage of 200 kV. The texture of the sample was determined using the Quantachrome Autosorb device and N<sub>2</sub> physisorption. A sample tube containing 50 mg sample was degassed at 200 °C for 6 h before being examined in liquid N<sub>2</sub> at −196 °C. Ex-situ and in-situ X-ray diffraction patterns (XRD) were obtained using a PANalytical X'Pert3 powder diffractometer with Cu K<sub>α</sub> radiation at the 30–80° 2θ at a scanning speed of 2°/min. Thermo Scientific Escalab 250Xi device was used to detect the materials' quasi-in-situ and ex-situ X-ray photoelectron spectra (XPS). Raman spectra were collected using a 532 nm excitation wavelength Bruker Optics Senterra Raman confocal microscope spectrometer. The Co-O bond force constant was calculated determined by the Raman shift of the bond according to the Hooke's law ( $\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$ ), where  $c$  is light velocity,  $\omega$  is the Raman shift (cm<sup>−1</sup>),  $\mu$  is effective mass, and  $k$  is the Co-O force constant [37].

#### 2.2.2. Chemisorption and DRIFTS

CO<sub>2</sub> pulse chemisorption was carried out on an AutoChem 2910 chemical adsorption instrument. Typically, 100 mg catalyst was inserted into a U-shaped sample tube. The sample was initially chilled at 120 °C for 1 h under Ar atmosphere (30 mL/min) and then cooled to 50 °C. Afterwards, a feed of 10% CO<sub>2</sub>/Ar was admitted by the pulse gas (loop volume of 526 μL) to saturate the catalyst surface. The physically adsorbed species were removed by purging Ar at the same temperature for 30 min. The desorption was started by ramping the sample temperature to 800 °C at a rate of 10 °C/min, and desorbed products were monitored with a Swiss OminiStar 300 mass spectrometer. H<sub>2</sub> pulse chemisorption was performed on a Zeton Altamira AMI-300 chemical adsorption instrument. 100 mg sample was loaded into a U-shaped tube. The catalyst was first pretreated at 120 ° for 2 h under Ar flow (30 mL/min). After cooling to 50 °C, a 10% H<sub>2</sub>/Ar mixture was admitted by pulse injection until adsorption saturation was reached. A thermal conductivity detector was used to detect the desorbed H<sub>2</sub>. H<sub>2</sub>-D<sub>2</sub> exchange experiments were carried out using an Autochem II 2920 chemisorption fitted with a mass spectrometer. 50 mg catalyst was inserted into U-shaped sample tube, pretreated for 1 h under Ar stream at 120 °C, and then chilled to room temperature. The treatment gas was changed to H<sub>2</sub>/D<sub>2</sub> mixture (31 mL/min, D<sub>2</sub>/H<sub>2</sub> = 1.07) once the baseline became steady. The temperature was raised to 250 °C with a ramping rate of 5 °C/min. The concentrations of gas-phase components (H<sub>2</sub>, D<sub>2</sub>, HD) were monitored with a mass spectrometer. In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out on the VERTEX 80 V FTIR spectrometer. For the in-situ DRIFTS studies of the RWGS reaction, the sample was initially purged with an Ar atmosphere at 120 °C for 30 min before introducing a stream of gas mixture (H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 72/18/10) and ramping the temperature

up to 500 °C at a rate of 5 °C/min.

### 2.3. Catalytic testing

The reversed water-gas shift reaction was performed in a fixed-bed plug flow reactor equipped with a gas chromatograph. Typically, 0.8 g of catalyst was placed at the center of a quartz tube with an inner diameter of 9 mm. The reaction gases of different H<sub>2</sub>:CO<sub>2</sub> ratios were introduced in the absence of pretreatment, with N<sub>2</sub> serving as the internal reference. The performances of various catalysts were evaluated at various reaction temperatures (300–500 °C) under atmospheric pressure. The outlet gas was analyzed online with an Agilent 7890 N GC chromatograph outfitted with a TDX-01 column and a thermal conductivity detector. The CO<sub>2</sub> conversion and product selectivity were estimated by the following equations.

$$\text{CO}_2 \text{ Conversion } (\%) = \frac{n\text{CO}_{2,\text{in}} - n\text{CO}_{2,\text{out}}}{n\text{CO}_{2,\text{in}}} \times 100\%$$

$$\text{CO Selectivity } (\%) = \frac{n\text{CO}_{\text{out}}}{n\text{CO}_{\text{out}} + n\text{CH}_4} \times 100\%$$

$$\text{CH}_4 \text{ Selectivity } (\%) = \frac{n\text{CH}_{4,\text{out}}}{n\text{CO}_{\text{out}} + n\text{CH}_{4,\text{out}}} \times 100\%$$

### 2.4. Theoretical methods

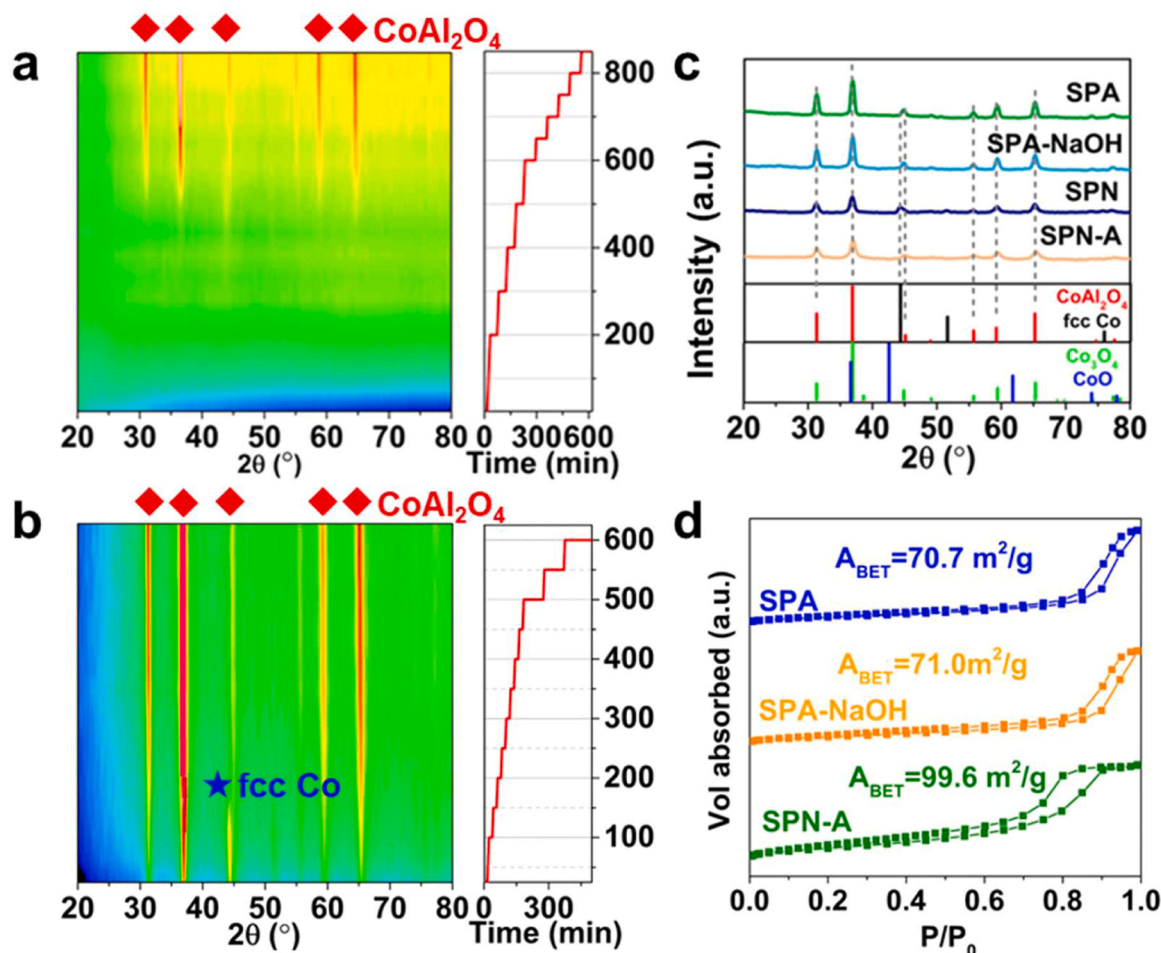
The theoretical calculation was completed with the Vienna Ab Initio

Simulation Package (VASP) using density functional theory (DFT) method. The key parameters were as follows. The standard pseudopotential of each element in projected augmented plane-wave (PAW) method was used. After energy test convergence, the cut-off energy was 450 eV. Because the system contains the magnetic element Co, spin polarization was used in the calculations. For all the structural optimization and property calculations, the convergence thresholds for the energy and force were 10<sup>−5</sup> eV and 0.02 eV/Å, respectively. The transition state was found by climbing image nudged elastic band (CI-NEB) method and confirmed by frequency analysis.

## 3. Results and discussion

### 3.1. Structural and compositional analyses

CoAl<sub>2</sub>O<sub>4</sub> spinels with different numbers of oxygen vacancies were prepared by the sol-gel method using corresponding metal nitrates as the precursors in the presence of propylene oxide (procedures illustrated in Fig. S1). To create more oxygen vacancies, the dried solids from the resulted gels were treated by different methods. Direct heating of the solids in flowing air or N<sub>2</sub> at 800 °C yielded the reference CoAl<sub>2</sub>O<sub>4</sub> spinels that were denoted as SPA and SPN, respectively. Additional two samples were derived by different treatments of these two compounds. SPN was further oxidized in air at 600 °C to yield a sample coded as SPN-A. Meanwhile, SPA was subject to NaOH etching at a mild temperature of 50 °C to create a new sample denoted as SPA-NaOH. Thermogravimetry (TG) was performed on the precursor Co-Al gel and the



**Fig. 1.** In situ XRD patterns of (a) Co-Al precursor in Air and (b) SPN in Air. (c) The XRD patterns of the SPA, SPA-NaOH, SPN and SPN-A catalysts, and the standard references of CoAl<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, CoO and fcc Co (vertical lines). (d) N<sub>2</sub> sorption isotherms of the different CoAl<sub>2</sub>O<sub>4</sub> spinel catalysts.

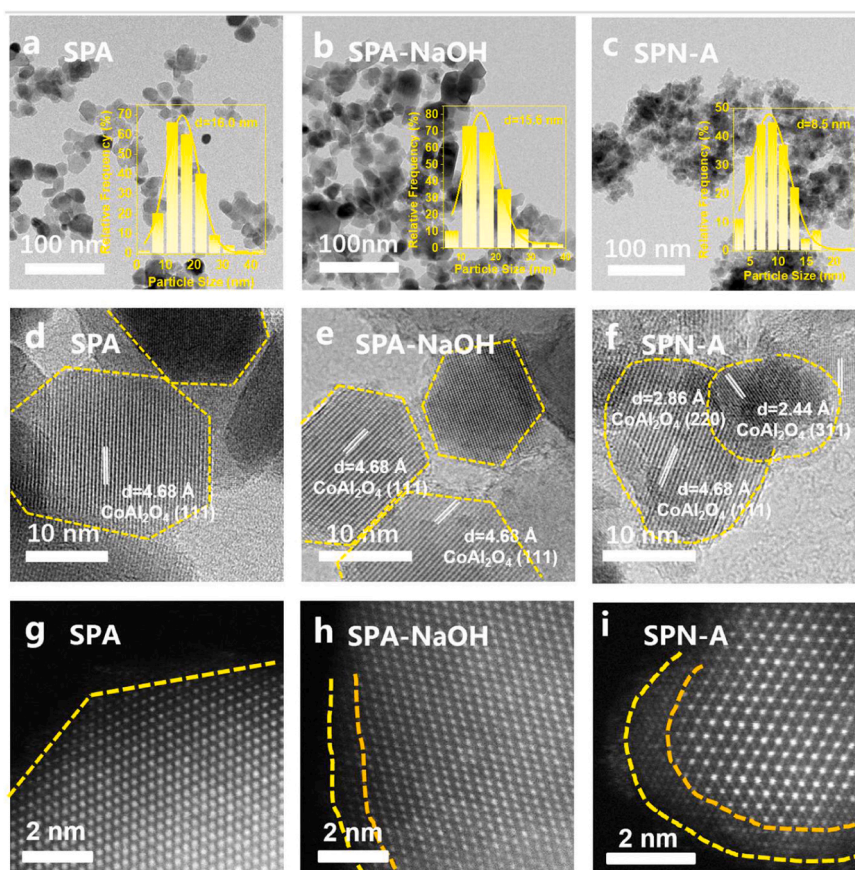


exhaust gas was detected by mass spectrometry to explore the chemical changes of the Co-Al precursor during the heat treatment process in Fig. S2. It was found that the  $H_2$  peak was found at a higher temperature during the programmed temperature rise under  $N_2$ , which may be due to the hydrogen element in the precursor being generated under oxygen-poor conditions, thus promoting the generation of  $Co^0$ . Under Air atmosphere, no  $H_2$  peak was found due to oxygen enrichment. The phase evolution of the solid gels during oxidation in air ambience was studied by in situ XRD with temperature-programmed heating mode (Fig. 1a). The characteristic diffraction patterns of  $CoAl_2O_4$  appeared at 400 °C after air oxidation, and these characteristics became more intense at the increasing temperatures up to 800 °C. In addition, the temperature-programmed phase evolution of SPN in air was also explored through in situ XRD (Fig. 1b). Differing from the diffraction patterns of SPA that showed the exclusively phase of  $CoAl_2O_4$ , metallic Co with fcc packing was evidenced for SPN, hinting the prominent impact of heating atmospheres on the phase transformation. The diffraction lines of the fcc Co gradually vanished and completely disappeared at 250 °C, accompanied with the formation of  $CoAl_2O_4$  spinels. Clearer single spectra before and after key changes in the in situ XRD spectrum are also provided in Fig. S3. To have a better comparison on the structures of the derived catalysts, their respective XRD patterns are presented in Fig. 1c. Although the XRD patterns for the catalysts clearly indicated the presence of only  $CoAl_2O_4$  crystallites (JCPDS card: 01-082-2248), still, noticeable differences were observable among these catalysts. While SPA-NaOH remained essentially unaltered in crystallinity as compared with SPA, SPN-A clearly displayed much lower diffraction intensities. The relative crystallinity of the different catalysts estimated by XRD patterns was in the order of SPA (100) > SPA-NaOH (97.1) > SPN-A (74.3). Next, the porosities of the above derived samples were analyzed

by  $N_2$  sorption (Fig. 1d and Table S1). While both SPA and SPA-NaOH possessed similar specific surface areas ( $S_{BET}$ ) of ca. 71  $m^2/g$ , SPN-A showed a higher value of 99.6  $m^2/g$ , implying that the post-oxidation maybe beneficial to generate more defective structures.

### 3.2. Electron microscopic studies

Having confirmed the compositions of the developed catalysts, combined electron microscopic investigations were performed to visualize the morphologies and particle sizes of the key samples (Fig. 2). The low-resolution TEM images showed more crystallized particles for both SPA and SPA-NaOH than SPN-A that displaying obvious amorphization (Fig. 2a-c). Statistic counting of the particles showed that the average sizes of  $CoAl_2O_4$  were 16.0, 15.6 and 8.5 nm, respectively, for SPA, SPA-NaOH, and SPN-A, thus corroborating well with the crystallite sizes estimated by Scherrer equation (Table S1). The size of the  $CoAl_2O_4$  catalyst often affects the catalytic performance including catalyst reduction and catalytic activity [38]. HRTEM images of the catalysts illustrate the distinctive lattice distances of 0.468, 0.286, and 0.244 nm (Fig. 2d-f), corresponding to the respective (111), (220) and (311) planes of  $CoAl_2O_4$  with SPA, SPA-NaOH and SPN-A catalysts. The characteristic lattice fringes of fcc Co (111) with  $d = 2.05$  nm were also observed in the SPN catalyst in Fig. S4, which is consistent with the in-situ XRD, indicating that the original reduction was achieved under  $N_2$  calcination. Furthermore, the two-dimensional projections of SPA generally present hexagonal grains with clear boundaries and complete lattice stripe orientation, implying that the SPA grains are similar to single crystals in the cubic system with perfect crystal facet. In contrast, for SPA-NaOH, due to the destruction of the crystalline integrity by alkaline etching, more defects appeared at the corners and edges of the



**Fig. 2.** Electron microscopic characterizations of the three  $CoAl_2O_4$  catalysts. (a-c) TEM images and the particle size distributions (insets) (d-f) HRTEM images, showing the representative lattice fringes of different Co species. (g-i) HAADF-STEM images, revealing the differences of defective sites on the particle edges.



hexagonal grains, and the boundaries became blurred albeit the lattice fringes in the grains remained intact (Fig. 2e). These observations confirmed that SPA-NaOH was mainly composed of single crystal grains, but many defects were formed on the grain surface or edge. For SPN-A, the grain boundaries became well-rounded and thus more disordered (Fig. 2f). High-index facets such as (220) and (311) coexisted with the typical (111) facets, forming nanoscale crystal defects such as steps, corners, and depressions, and thus confirming polycrystalline characteristics of the grains [39,40]. HAADF-STEM was further applied to visualize the detailed defective structures (Fig. 2g-i). The grain boundaries of SPA-NaOH and SPN-A were incomplete and disordered layers with a thickness of 1–2 nm were observed, which can be attributed to the exfoliation of surface lattice oxygen during the base or oxidation processing [41]. In addition, SEM images and EDS mapping of different catalysts revealed that all the catalysts were evenly distributed (Figs. S5–S6).

### 3.3. Oxygen vacancies

Since the catalytic reaction occurs on the surface, the surface properties of the catalysts were studied by XPS (Fig. 3a). The Co 2p XPS spectra of the three pre-reaction catalysts are shown in Fig. S7. Only the characteristic binding energy peak of  $\text{Co}^{2+}$  was found. Comparison on the O 1s XPS spectra of the three catalysts revealed that the peak of SPN-A noticeably shifted towards higher binding energy as compared with the other two catalysts. Following the previous literature [32], the O 1s envelopes were deconvoluted into two peaks: lattice oxygen ( $\text{O}_\text{L}$ ) on the surface and adsorbed oxygen on the surface ( $\text{O}_\text{A}$ ), and the formation of oxygen vacancies due to  $\text{O}_2$  adsorption. The fitting results of the three samples revealed that the  $\text{O}_\text{A}/(\text{O}_\text{A}+\text{O}_\text{L})$  ratios follow the order of  $\text{SPN-A} > \text{SPA-NaOH} > \text{SPA}$ . Therefore, the formation of more oxygen vacancies in SPN-A with a more disordered spinel structure corresponds to the irregular surface defects of the catalyst. To further study the crystal structure of  $\text{CoAl}_2\text{O}_4$  catalysts, Raman spectroscopy was performed (Fig. 3b).  $\text{CoAl}_2\text{O}_4$  typically presents five active Raman models:  $\text{F}_{2g}$  (201, 516, 615  $\text{cm}^{-1}$ ),  $\text{E}_g$  (406  $\text{cm}^{-1}$ ) and  $\text{A}_{1g}$  (705  $\text{cm}^{-1}$ ) [39,42]. Among them, the  $\text{F}_{2g}$  (1) mode belongs to Co/Al-O<sub>4</sub> tetrahedral translation. The  $\text{E}_g$  mode corresponds to the symmetric bending motion of the oxygen atom in the tetrahedron, and its position has a decent association with the cation radius of the 8a site. [43]. The Co/Al-O asymmetric stretching vibrations in the tetrahedral sites are responsible for the  $\text{F}_{2g}$  (2) mode. The  $\text{F}_{2g}$  (3) mode is the antisymmetric stretching mode of the tetrahedral unit and the asymmetric bending motion of the oxygen bonded to the tetrahedral cation. The Co/Al-O stretching vibration in the octahedron is related to the  $\text{A}_{1g}$  mode.  $\text{F}_{2g}$  (2) can be viewed as the evidence for judging the existence of metal-O bonds in spinels [43]. It was found that the  $\text{F}_{2g}$  (2) peaks of SPA, SPA-NaOH and SPN-A catalysts located at 522.8, 520.9 and 517.4  $\text{cm}^{-1}$  respectively, indicating red-shifting with the increasing oxygen vacancies. According to the Raman shift of the Co-O bond, the

bond force constant (K) of Co-O bond was calculated, following the order of  $\text{SPN-A} < \text{SPA-NaOH} < \text{SPA}$  (Fig. 3b). An interesting quasi-linear relationship was established between the relative  $\text{O}_\text{A}$  content and the bond force constant (Fig. S8), illustrating that the increasing  $\text{O}_\text{A}$  concentration leads to the weakening of the Co-O bond of the spinel catalyst [37].

### 3.4. $\text{CO}_2$ hydrogenation

The  $\text{CoAl}_2\text{O}_4$  spinels with different structures were evaluated for  $\text{CO}_2$  hydrogenation reaction in a fixed bed reactor at 300–500 °C (Fig. 4a). SPA displayed a moderate  $\text{CO}_2$  conversion with almost full CO selectivity at 400 °C. Both the conversion and  $\text{CH}_4$  selectivity increased slightly on SPA-NaOH. In contrast, the  $\text{CO}_2$  conversion significantly improved over SPN-A and  $\text{CH}_4$  became the predominate product with a higher selectivity of 90%. The impacts of temperature and  $\text{H}_2/\text{CO}_2$  ratio on the product selectivity and  $\text{CO}_2$  conversion were further evaluated. The CO selectivity of SPA catalyst kept at ~100% in the full temperature range of 300–500 °C (Fig. 4g) and remained stable in the 100 h time-on-stream (Fig. 4b). The stability test of SPN-A reveals that the  $\text{CH}_4$  selectivity increased and became stable after 15 h (Fig. 4b). The CO selectivity of SPN-A catalyst increased slightly as the temperature increased from 400 to 500 °C, but  $\text{CH}_4$  was still the major product (Fig. 4g). The effect of  $\text{H}_2/\text{CO}_2$  ratio on the catalytic performance was presented in Fig. 4h. As expected, a higher  $\text{H}_2/\text{CO}_2$  ratio promoted  $\text{CO}_2$  conversion, but the impact on product distribution varied. The CO selectivity remained ~100% on SPA at  $\text{H}_2/\text{CO}_2 = 4$ , whereas  $\text{CH}_4$  formation was enhanced over SPA-NaOH and SPN-A with the increasing  $\text{H}_2/\text{CO}_2$  ratio. Subsequently, the electronic states of the Co species in different catalysts after the reaction were detected. The XRD patterns of the spent catalysts show that the  $\text{CoAl}_2\text{O}_4$  spinel was stable on SPA after the reaction (Fig. 4c). In contrast, the spent SPN-A showed the characteristic peak of fcc Co in addition to  $\text{CoAl}_2\text{O}_4$ , indicating that the active centers of the catalyst might comprise both nanoparticle of  $\text{Co}^0$  and  $\text{CoAl}_2\text{O}_4$  during the reaction. Quasi in situ XPS investigation of two spent catalysts further revealed that SPN-A was partially reduced to metallic Co nanoparticle, whereas the  $\text{Co}^{2+}$  species on SPA remained stable in the  $\text{H}_2/\text{CO}_2$  reaction atmosphere (Fig. 4d) and it was found that the spent catalyst has more oxygen vacancies (Fig. S9). These results were further corroborated by HRTEM analyses (Fig. 4e–f), confirming the exclusive presence of  $\text{CoAl}_2\text{O}_4$  on SPA, but small metallic Co nanoparticles coexisting with  $\text{CoAl}_2\text{O}_4$  on SPN-A. The SPN-A catalyst was tested after  $\text{H}_2$  reduction to demonstrate the active center which produced  $\text{CH}_4$  (Fig. S10). It was discovered that the  $\text{CH}_4$  selectivity could be raised to 98%, thus confirming that active center was  $\text{Co}^0$  species obtained by  $\text{CoAl}_2\text{O}_4$  reduction. The reaction-induced partial phase transition from  $\text{CoAl}_2\text{O}_4$  to  $\text{Co}^0$  in SPN-A can well explain the induction phenomenon during the stability test (Fig. 4b).

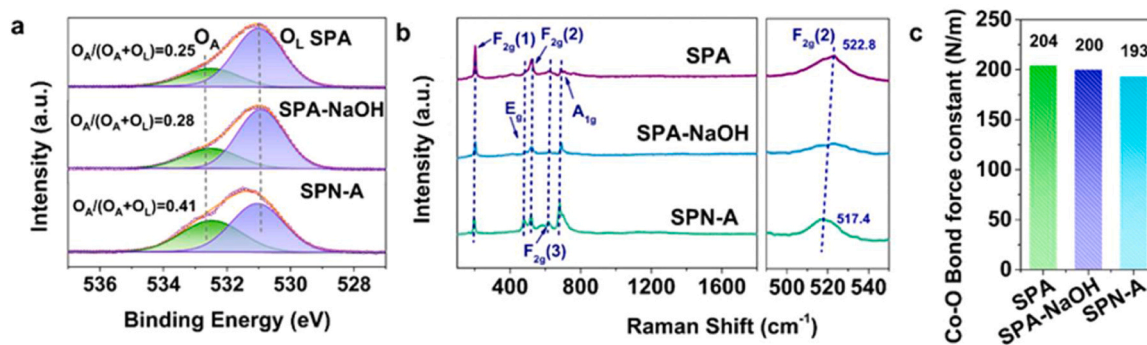
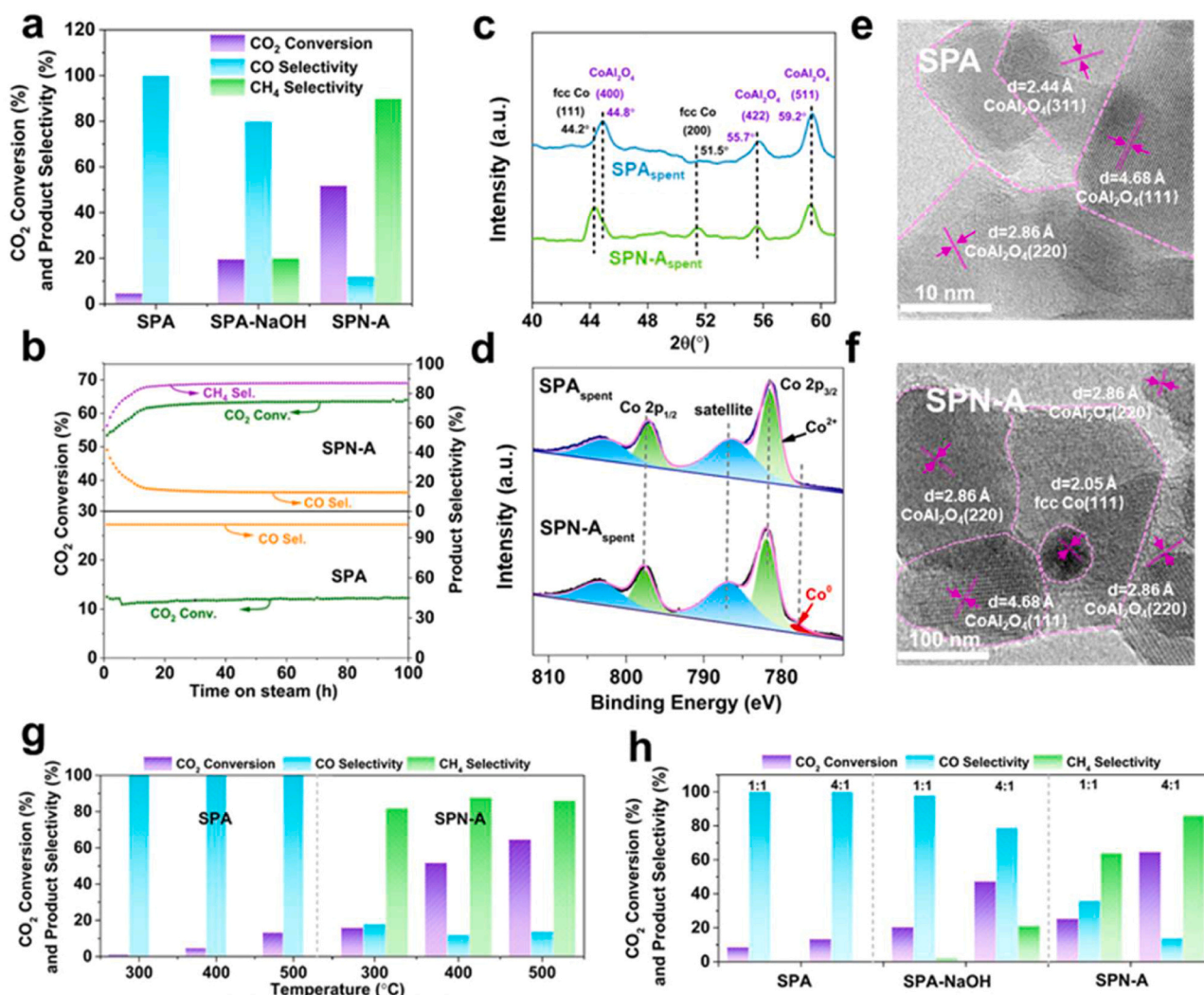


Fig. 3. (a) The O 1s XPS spectra, and (b) Raman spectra of the different  $\text{CoAl}_2\text{O}_4$  spinel catalysts. (c) The calculated Co-O bond force constants based on the Hooke's law.



**Fig. 4.** (a) Catalytic performance of CoAl<sub>2</sub>O<sub>4</sub> catalysts in CO<sub>2</sub> hydrogenation. (Reaction conditions: 400 °C, 0.1 MPa, 5000 mL·g<sup>-1</sup>·h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 72/18/10). (b) 100 h time-on-stream of the SPA catalyst (Reaction condition: 500 °C, 0.1 MPa, 5000 mL·g<sup>-1</sup>·h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 72/18/10). (c) XRD patterns of the different spent catalysts. (d) Co 2p XPS spectra of the spent catalysts. TEM images of the spent (e) SPA and (f) SPN-A catalysts. CO<sub>2</sub> conversion and product selectivity at different (g) temperatures (0.1 MPa, 5000 mL·g<sup>-1</sup>·h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 72/18/10) and (h) H<sub>2</sub>/CO ratios (500 °C, 0.1 MPa, 5000 mL·g<sup>-1</sup>·h<sup>-1</sup>).

### 3.5. Reduction and chemisorption properties

H<sub>2</sub>-TPR profiles of the different CoAl<sub>2</sub>O<sub>4</sub> catalysts were recorded and represented in Fig. 5a. No reduction peak was observed on SPA up to 700 °C, while two high-temperature reduction peaks were found on SPN-A and SPA-NaOH, which can be attributed to the reduction of surface and bulk Co species, respectively [44,45]. The reduction temperatures for SPN-A catalyst were 411 and 520 °C, respectively. These peaks shifted to 520 and 780 °C for SPA-NaOH. According to the previous literature [46], the shifting toward higher reduction temperature could be ascribed to the presence of stable oxide species that are hard to reduce. The higher portion of the low-temperature reduction peak in SPN-A thus corroborates with the most abundant oxygen vacancies as revealed by our combined characterizations. In addition, H/D exchange experiments showed that the light-off curves of HD formation shifted to the lower temperatures in the order of SPA > SPA-NaOH > SPN-A (Fig. 5b). The results show that the increase in oxygen vacancies enhances the ability to activate H<sub>2</sub>, which promotes catalyst reduction, and the catalytic products are more inclined to further hydrogenation. To this end, H<sub>2</sub> pulse adsorption experiments were conducted to evaluate the H<sub>2</sub> adsorption/activation ability of the different catalysts [47,48]. The H<sub>2</sub> pulse adsorption experiments of the catalysts show that the

increase in oxygen vacancies promotes the adsorption of H<sub>2</sub> (Fig. 5c). For instance, the H<sub>2</sub> adsorption capacity of SPA was 10 μmol/g and that of SPN-A increased to 30 μmol/g. Similar results were acquired for the CO<sub>2</sub> adsorption experiments. The CO<sub>2</sub> adsorption quantities were determined to be 4.6, 19.2 and 33.9 μmol/g, respectively, for SPA, SPA-NaOH and SPN-A (Fig. 5d). Note that the different CO<sub>2</sub> adsorption intensities between these catalysts can affect the activation of hydrogen, thus further influencing the adsorption/desorption of active intermediates and product selectivity [34,49].

### 3.6. In situ DRIFT study

In situ DRIFTS was performed under RWGS reaction conditions to explore the kinetic fingerprints (Fig. 6 and S11), and the corresponding band assignments were listed in Table S2. In a mixed atmosphere (H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 72/18/10) the sample temperature was elevated over SPA (Fig. 6a), SPA-NaOH (Fig. 6b) and SPN-A (Fig. 6c), respectively. On SPA and SPA-NaOH, the formations of COOH\* (carboxylates) and CO<sub>3</sub>\* intermediates were first observed at 1657 and 1434 cm<sup>-1</sup>, indicating that the catalysts first underwent CO<sub>2</sub> adsorption to generate CO<sub>3</sub>\* and COOH\* intermediates. The peak intensities of two intermediates decreased significantly with the increasing temperatures, accompanied

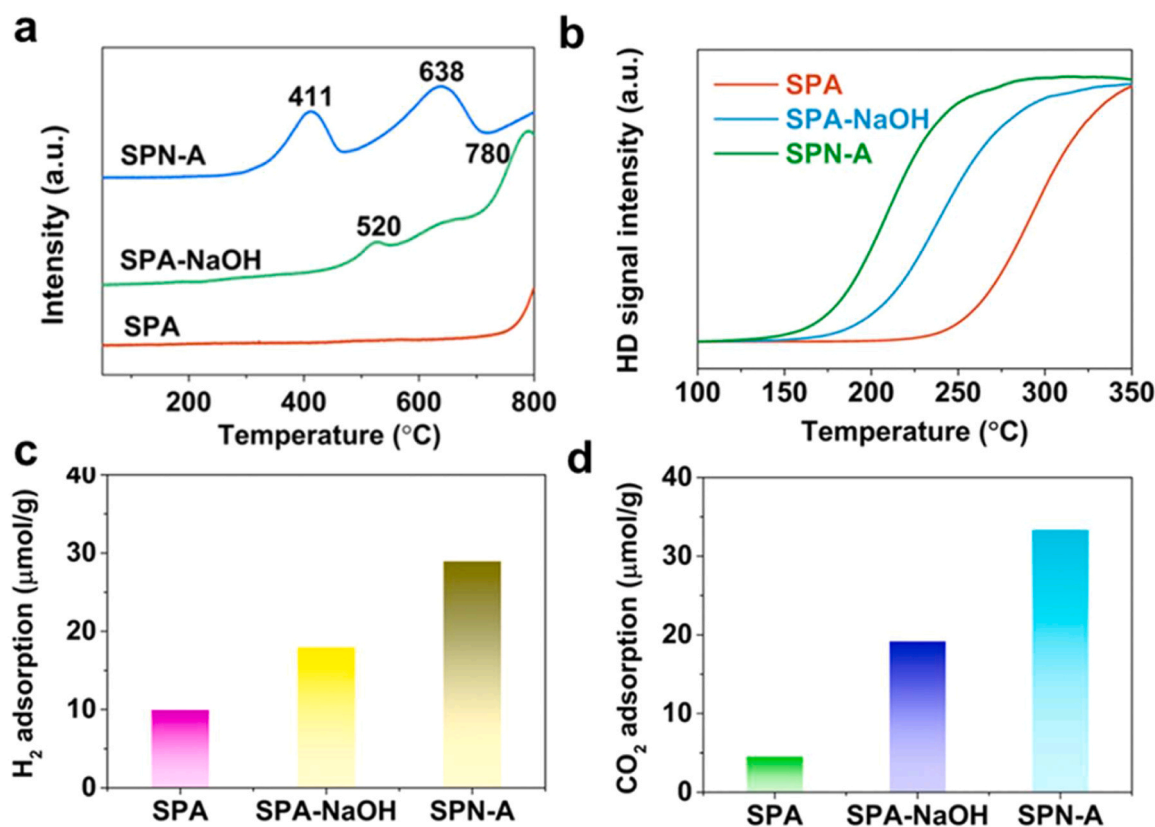


Fig. 5. (a) H<sub>2</sub>-TPR, (b) H<sub>2</sub>-D<sub>2</sub> exchange, (c) H<sub>2</sub> adsorption and (d) CO<sub>2</sub> adsorption on the three CoAl<sub>2</sub>O<sub>4</sub> catalysts.

by the gradual formation of CO, which indicated that the intermediates COOH\* and CO<sub>3</sub>\* were gradually consumed at higher temperatures to generate gas-phase CO [50]. A comparison on the temperatures corresponding to the release of gas-phase CO between SPA and SPA-NaOH (approximately 420 and 350 °C, respectively) reveals a lower temperature for SPA-NaOH, agreeing well with the higher hydrogenation activity as described previously. In addition, with the further increasing of temperatures, the C-H stretching vibration bands of HCOO\* (formates) intermediates at 2762, 2903 and 2997 cm<sup>-1</sup> and the C-O stretching vibrations at 1593 and 1303 cm<sup>-1</sup> were also observed, indicating that the HCOO\* intermediates were more difficult to generate and desorb than the COOH\* intermediates and in good agreement with the earlier studies [27,51]. In the Ar purge experiments, it was found that the HCOO\* intermediate was more difficult to desorb on SPN-A and SPA-NaOH, and the characteristic peak of HCOO\* was still observable after 30 min purging, indicating that the generated HCOO\*-intermediate was difficult to undergo further reactions (Fig. S12). On SPN-A, the generation and consumption of COOH\* with increasing temperatures were also evidenced, accompanied with the release of CO. Nonetheless, in addition to the gas-phase CO, the surface-bound CO\* intermediate species appeared at 2006 cm<sup>-1</sup> at a low temperature of 150 °C. This CO\* intermediate red-shifted to 1952 cm<sup>-1</sup> when the temperature increased. In addition, the characteristic bands of the HCOO\* intermediates appeared at 200 °C, but the intensities decreased with the increasing temperatures, accompanied with the formation of meteorological CH<sub>4</sub> (3014, 1226 cm<sup>-1</sup>). Therefore, the formation of CH<sub>4</sub> may be from CO\* and HCOO\*. Ar purge experiments further showed that the CO\* was easier to desorb than HCOO\*, hinting that CH<sub>4</sub> was more likely originated from the hydrogenation of the CO\* intermediates.

### 3.7. Mechanistic insights

To clarify the relationships between different oxygen vacancies of CoAl<sub>2</sub>O<sub>4</sub> and the selectivity to CO and CH<sub>4</sub> during CO<sub>2</sub> hydrogenation, DFT calculations were performed, with the focus placed on the adsorption of key intermediate species generated in CO<sub>2</sub> hydrogenation and the reaction mechanism. Based on our thorough characterizations, three different Co catalyst models were constructed for SPA, SPA-NaOH and SPN-A, considering the different cobalt compositions (nano-particle metallic Co and CoAl<sub>2</sub>O<sub>4</sub>) and CoAl<sub>2</sub>O<sub>4</sub> with or without oxygen vacancies (Figs. S13-S14). For the rational selection of oxygen vacancy-bearing spinels, the formation energies were first computed for the different faceted CoAl<sub>2</sub>O<sub>4</sub> with oxygen defects (Fig. S13) and Table S3). The (100) facet with the lowest energies of 2.5 eV was thermodynamically more favorable than the (111) and (110) facets (4.26 and 3.76 eV, respectively), and thus was chosen for further consideration. The full reaction coordinates of the simulated elemental steps of CO<sub>2</sub> hydrogenation over CoAl<sub>2</sub>O<sub>4</sub>(100), CoAl<sub>2</sub>O<sub>4</sub>-O<sub>v</sub>(100) and Co(111) were presented in Fig. 7. The CO<sub>2</sub> adsorption at both CoAl<sub>2</sub>O<sub>4</sub>(100) and CoAl<sub>2</sub>O<sub>4</sub>-O<sub>v</sub>(100) was exothermic and more favorable for the later, agreeing well with the CO<sub>2</sub> chemisorption analysis. Afterwards, the activation of CO<sub>2</sub>\* underwent an upwards slope with the energy barriers of 1.18 and 1.09 eV, respectively. The subsequent hydrogenation of the adsorbed CO<sub>2</sub>\* and H-assisted dissociation can generate either HCOO\* or COOH\* intermediates. Although both routes are energy-demanding irrespective of the oxygen vacancies, the COOH\* route is kinetically more favorable with much lower barriers, particularly for CoAl<sub>2</sub>O<sub>4</sub>-O<sub>v</sub>(100) with the lowest barrier of only 0.34 eV. After passing another transient state (TS), these adsorbed COOH\* intermediates further dissociate into CO\* with only 0.16–0.35 eV. Due to the relatively weak adsorption of CO\*, it will directly desorb into gas-phase CO instead of going further hydrogenation that requires higher energy input. For Co(111), the energy barrier for the direct dissociation of CO<sub>2</sub> to form CO\* is



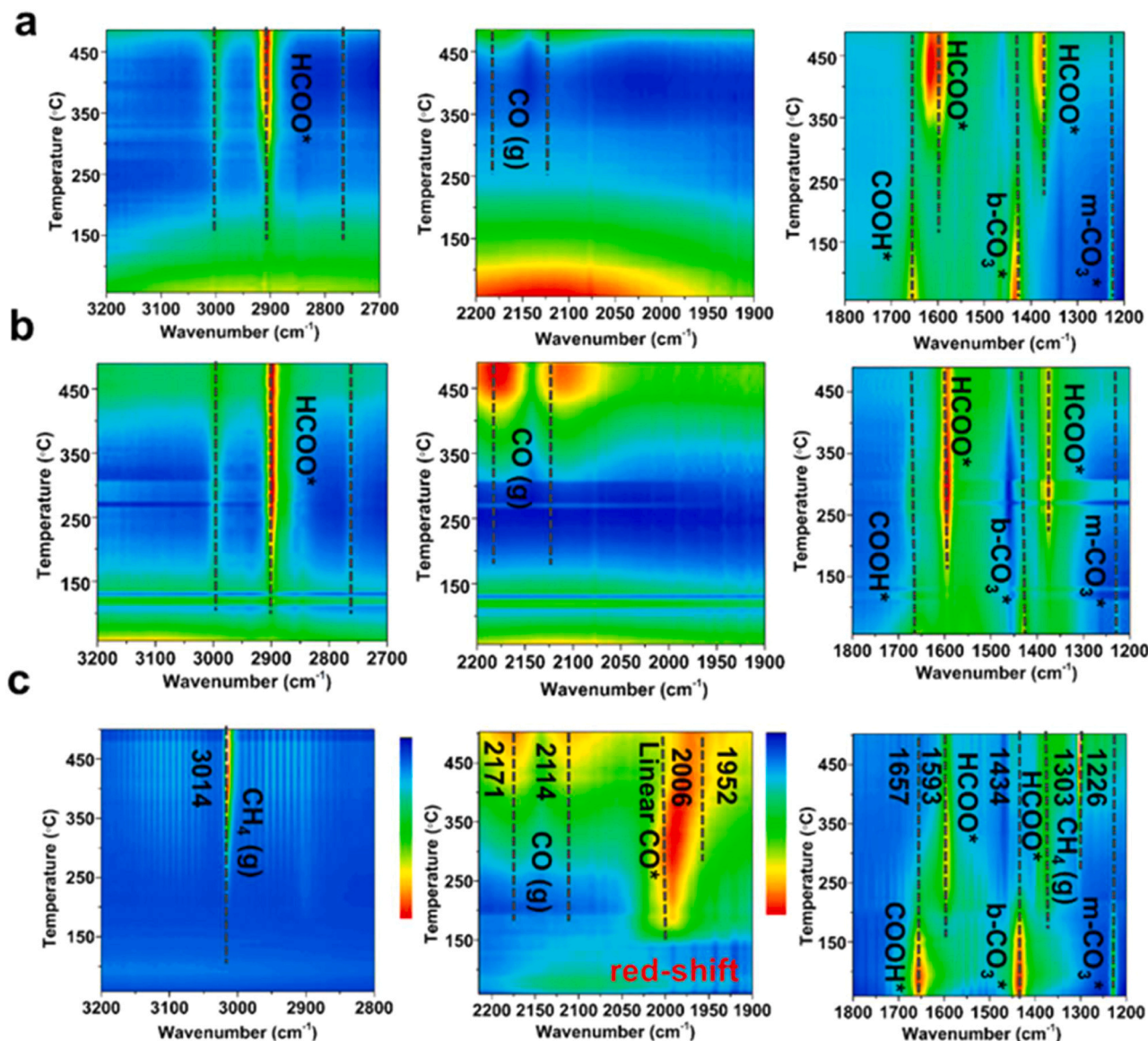


Fig. 6. In situ DRIFTS spectra of (a) SPA, (b) SPA-NaOH and (c) SPN-A catalysts after exposure to the gas mixture ( $\text{H}_2/\text{CO}_2/\text{N}_2 = 72/18/10$ ) at different temperatures during  $\text{CO}_2$  hydrogenation.

lower as compared with  $\text{COOH}^*$  and  $\text{HCOO}^*$ , and the energy barrier for further hydrogenation of  $\text{CO}^*$  is lower than the desorption energy barrier, so it is easier for further hydrogenation to  $\text{CH}_4$  (Fig. 7c). The full adsorption configurations on the three model catalysts are shown in Figs. S15-S17 for reference. In general, the DFT calculations are in good agreement with the activity and product selectivity of the different Co species in the  $\text{CO}_2$  hydrogenation experiment.

### 3.8. Roles of oxygen vacancies

The multifaceted roles of oxygen vacancies in  $\text{CO}_2$  hydrogenation have been reported by different research groups [10,13,17]. Even so, the mechanistic origins behind these observed phenomena are mainly speculated. By constructing three  $\text{CoAl}_2\text{O}_4$  spinels with varying numbers of oxygen vacancies, their critical roles in hydrogenation performance were systematically assessed in this study as summarized in Fig. 8. In the earlier literatures, the oxophilic nature of oxygen vacancies were reported to enhance the adsorption of  $\text{CO}_2$ , and subsequently the hydrogenation was facilitated at the adjacent metal atoms [32]. These conclusions were fully supported by our  $\text{CO}_2$ -TPD and catalytic

evaluations. Nonetheless, the enhanced  $\text{CO}_2$  adsorption might not be the only reason accounting for the improved activity. In fact, our DFT calculations revealed only slight differences in the  $\text{CO}_2$  activation between  $\text{CoAl}_2\text{O}_4(100)$  with or without oxygen vacancies (barriers of 1.09 and 1.18 eV, respectively). In stark contrast, the H-assisted activation of  $\text{CO}_2^*$  to  $\text{COOH}^*$ , which is the rate-limiting step on  $\text{CoAl}_2\text{O}_4(100)$  with a high barrier of 1.37 eV, is significantly favored on  $\text{CoAl}_2\text{O}_4(100)\text{-O}_v$  with a mild barrier of only 0.34 eV. This suggested that the splitting of molecular  $\text{H}_2$  is also crucial to the above elemental step. This speculation was indeed supported by our  $\text{H}_2$ -TPD and H/D exchange experiments, i. e., the  $\text{H}_2$  adsorption and activation propensities scale with the increasing numbers of oxygen vacancies. In addition, the increasing oxygen vacancies were found to impact the reducibility of the  $\text{Co}^{2+}$  species that has scarcely been addressed in early works. Albeit  $\text{CO}_2$  hydrogenation activity can be promoted on oxygen vacancy-rich  $\text{CoAl}_2\text{O}_4$  spinels, while product selectivity from  $\text{CO}$  to  $\text{CH}_4$  was evidenced on SPN-A with the most abundant oxygen vacancies. This was clearly ascribed to the reduction of  $\text{CoAl}_2\text{O}_4$  spinels to metallic Co species in the hydrogenation atmosphere, which has been confirmed by the characterization of the post-reaction catalyst. Supported by both in situ

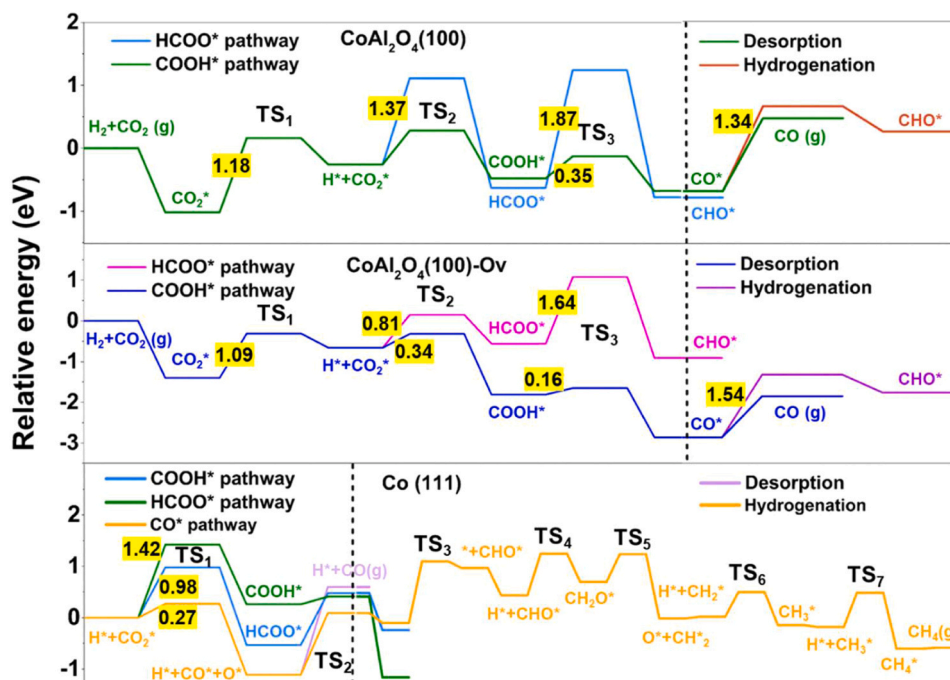


Fig. 7. The full reaction coordinates of CO<sub>2</sub> hydrogenation on the different Co-based model catalysts: (a) CoAl<sub>2</sub>O<sub>4</sub>(100), (b) CoAl<sub>2</sub>O<sub>4</sub>(100)-Ov, and (c) Co(111).

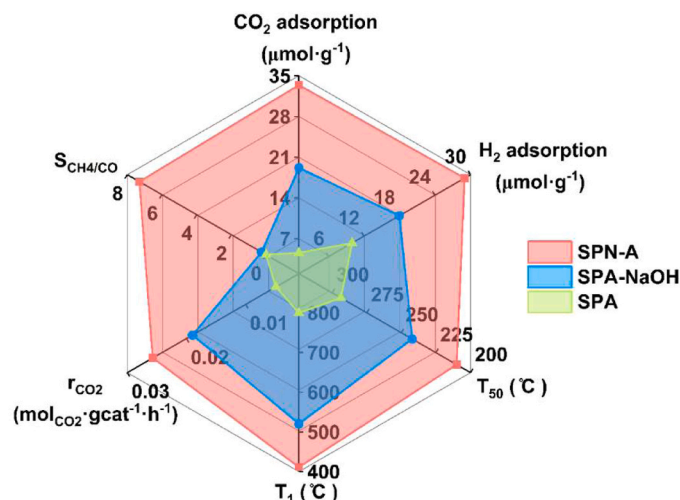


Fig. 8. Performance descriptors in CO<sub>2</sub> hydrogenation on different Co-based catalysts: SPA, SPA-NaOH and SPN-A. The pink, blue and green shaded areas represent the descriptors for SPN-A, SPA-NaOH and SPA, respectively. T<sub>50</sub>: the temperature corresponding to 50% HD exchange activity; T<sub>1</sub>: the temperature of the first reduction peak in H<sub>2</sub>-TPR, where 800 °C for SPA represents greater than 800 °C; r<sub>CO<sub>2</sub></sub>: hydrogenation rate; S<sub>CH<sub>4</sub>/CO</sub>: the ratio of CH<sub>4</sub> selectivity to CO selectivity.

DRIFT and DFT calculations, these in situ generated Co<sup>0</sup> species was proved to facilitate the direct hydrogenation of the CO<sub>2</sub>\* to CO\* instead of the COOH\* on CoAl<sub>2</sub>O<sub>4</sub> irrespective of the oxygen vacancies, thus providing the mechanistic basis for the underlying reaction mechanisms. On the other hand, the strongly promoted reduction behaviors of CoAl<sub>2</sub>O<sub>4</sub> spinels by the creation of oxygen vacancies might be associated with the greatly enhanced H<sub>2</sub> adsorption and activation. The recent report by Bao et al. [36] suggested the remote H-spillover from ZnO to Co<sub>3</sub>O<sub>4</sub> which promoted the reduction of the latter. However, such phenomenon was not detected when small Co<sub>3</sub>O<sub>4</sub> particles were constrained by the ZnO-Co<sub>3</sub>O<sub>4</sub> interface. We speculate that the less constrained Co<sup>2+</sup>

species due to the creation of oxygen defects led to easier reduction of CoAl<sub>2</sub>O<sub>4</sub> spinels.

#### 4. Conclusions

In this study, we have developed three Co-Al spinel catalysts containing varying numbers of oxygen vacancies by a sol-gel method and different post-treatments. The detailed structural and compositional information as well as the differences in oxygen vacancies were fully characterized by combined microscopic and spectroscopic techniques. The impacts of the oxygen vacancies on their CO<sub>2</sub> hydrogenation performances were systematically evaluated. These experiments enabled to acquire new fundamental insights into the unveiled mechanistic of the oxygen vacancy-dependent catalytic responses, i.e., exclusive CO formation with lower activity on perfect spinel crystals possessing least oxygen vacancies, and highly active but CH<sub>4</sub>-selective spinels with overwhelmingly rich oxygen vacancies. This unusual phenomenon can be associated with the different stabilities of the Co<sup>2+</sup> species that were more susceptible to reduction during working conditions wherein the O defective sites enriched the adsorption and activation of H<sub>2</sub>. Therefore, there is a complex interplay between the oxygen vacancies of the spinels, the catalyst stability (under reductive atmospheres), and the hydrogenation performance, which ultimately calls for more careful catalyst design.

#### CRedit authorship contribution statement

**Yihui Li:** Investigation, Data curation, Conceptualization, Formal analysis, Methodology, Visualization, Writing - original draft. **Ziang Zhao:** Supervision, Conceptualization, Writing - review & editing. **Zhao Min:** Formal analysis, Investigation. **Hejun Zhu:** Project administration, Supervision, Validation, Writing - original draft. **Xinzheng Ma** and **Zheng Li:** Data curation. **Wei Lu:** Methodology, Conceptualization. **Xingkun Chen:** Formal analysis. **Linbin Ying:** Density functional theory calculations. **Ronghe Lin:** Formal analysis, Writing - review & editing. **Yu Meng:** Density functional theory calculations. **Yuan Lyu:** Formal analysis, Investigation. **Li Yan:** Project administration, Resources. **Yunjie Ding:** Supervision, Project administration, Writing -



review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

## Acknowledgements

We greatly appreciate the financial support by the National Natural Science Foundation of China (No. 22002151, No. 22162028 and No. 22102147), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA 29050300), National Key Research and Development Program of China (No. 2023YFB4103100), Young Elite Scientists Sponsorship Program by CAST (No. 2023QNRC001), Zhejiang Provincial Natural Science Foundation of China (No. LQ21B030009) and Key Research and Development Program of Shaanxi (No. 2022GY-204). We acknowledge Professor Yuefeng Liu for advices and discussions on the manuscript.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.123824](https://doi.org/10.1016/j.apcatb.2024.123824).

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